

PATENT SPECIFICATION

(11) 1355 233

1355 233

- (21) Application No. 45831/71 (22) Filed 1 Oct. 1971
 (31) Convention Application Nos. 90134, 90153 and 90155
 (32) Filed 16 Nov. 1970 in
 (33) United States of America (US)
 (44) Complete Specification published 5 June 1974
 (51) International Classification C08G 41/00; A61K 7/06, 7/16;
 C11D 3/48, 9/50
 (52) Index at acceptance



C3R 33C11 33C12 33C13M 33C13S 33C16 33C25 33C29
 33C2A 33C33B 33C4 33C6B 33C6X 33C7 33C8R
 33C9A 33C9N 33K 33L2A 33L2X 33P

A5B 771 772 774

C5D 6A1 6B10B 6B11C 6B12A 6B12B 6B12B3 6B12E
 6B12F1 6B12F2 6B12G1 6B12G2A 6B12G6 6B12H
 6B12K2 6B12L 6B12M 6B12P 6B13 6B4
 6B6 6C8 6C9

(54) COSMETIC COMPOSITIONS AND THEIR USE

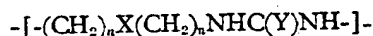
- (71) We, COLGATE-PALMOLIVE COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 300 Park Avenue, New York, New York 10022, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to cosmetic compositions and their use.

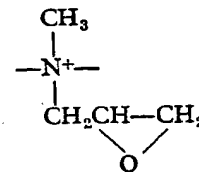
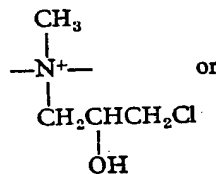
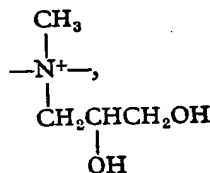
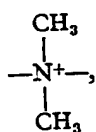
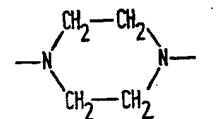
- 15 The term "cosmetic compositions" is used herein in a broad sense as mean compositions for application to the skin, hair and oral cavity for aesthetic functions, which compositions may also perform other functions, namely inhibition of the growth of various micro-

organisms, such as *Staphylococcus aureus*, *Pityrosporum ovale* and oral streptococci, modification of the surface of the hair and of the skin to improve the feel and the slip such as by removing roughness and reducing sloughing of the outer layers of skin, and inhibition of formation of calculus on and caries in the teeth. 20 25

According to one aspect of the invention a method of improving the condition of the hair, skin or oral cavity comprises applying thereto a composition comprising (I) 0.05 to 10% by weight of a water-soluble aminopolyureylene (hereinafter sometimes abbreviated as APU) resin having a molecular weight in the range from 300 to 100,000 and having the following repeating unit:— 30 35



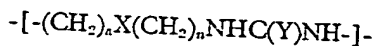
wherein X is $-\text{NH}-$, C_{1-22} alkyl
 $-\text{N}-$



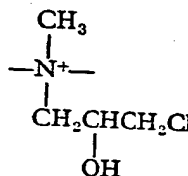
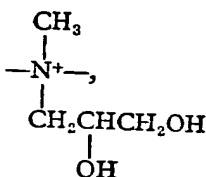
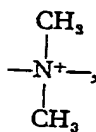
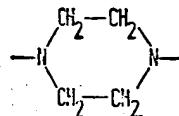
Y is O or S, and n is 2 or 3;

and (II) a compatible, nontoxic vehicle.

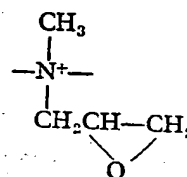
According to another aspect of the invention a cosmetic composition (as defined above) comprises (I) 0.05% to 10% by weight of a water-soluble aminopolyureylene resin having a molecular weight in the range 300 to 100,000 and having the following repeating unit:



wherein X is $-\text{NH}-$, C_{1-22} alkyl
 $-\text{N}-$



or



Y is O or S, and n is 2 or 3;

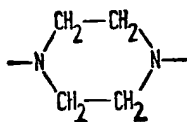
and (II) 90% to 99.5% by weight of a compatible, nontoxic vehicle which includes at least one member selected from aqueous C_2-C_3 alcohols, water-soluble synthetic organic detergents and water-insoluble polishing agents.

Preferred APU resins have an average molecular weight in the range of 1,000 to 20,000.

Thus, suitable APU resins include both the polyurea- and the polythiourea-containing compounds. Preferred APU resins have a repeating unit where Y is oxygen, n is 3, and X is



alkyl or



A particularly preferred resin is the reaction product of equimolar quantities of N-methyl, bis(3-aminopropyl) amine and urea, having a molecular weight of about 4,300.

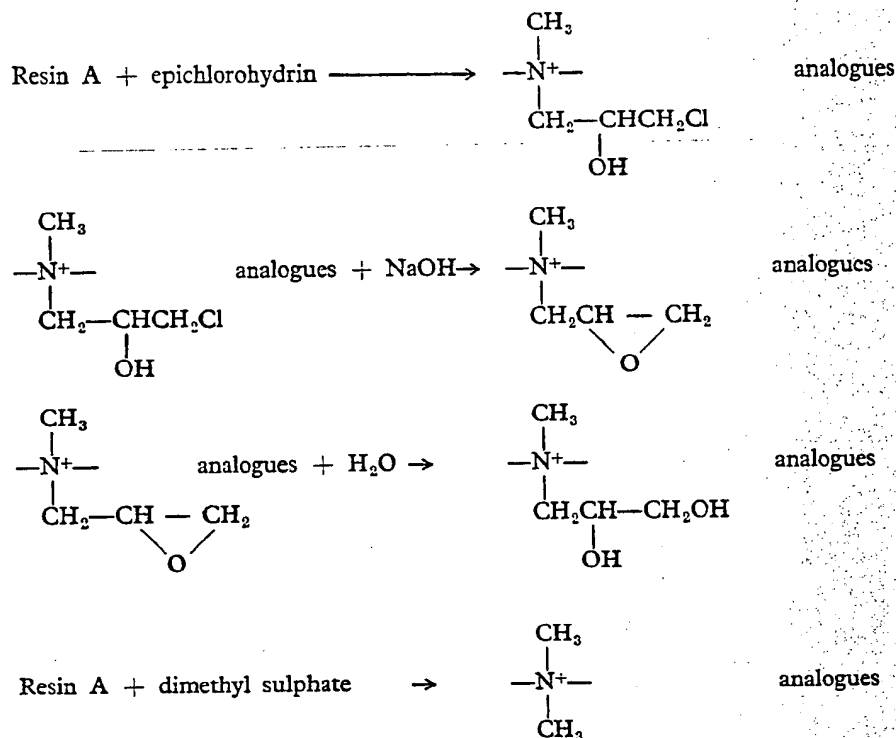
The molecular weight of the APU resins is based upon aqueous gel permeation chromatographic analysis.

The separation is carried out in oxalic acid solution, adjusted to pH 3.5, on three Corning controlled-pore glass columns (nominal pore sizes 175, 125, and 75 Å) in series. Detection is by differential refractometer. Reference compounds are dextran polysaccharides of molecular weights of 150,000, 110,000, 40,000 and 10,000 and sucrose and galactose.

The APU polymers which can be used in the compositions of this invention are prepared by reacting, for example, 145 grams of N-methyl bis(3-aminopropyl) amine (1. mole) and 60 grams of urea (1.0 mole) in a 3-necked flask equipped with a thermometer, mechanical stirrer, condenser and nitrogen sparge tube. Nitrogen is bubbled slowly through the solution throughout the course of the reaction. The solution is heated to 140°C over a 20-minute period when ammonia begins to evolve. The solution is further heated to 250°C over a 30-minute period and allowed to cool. The product is a hard, resinous powder (Resin A) having a molecular weight of about 4300. An aqueous solution containing 47.6 per cent solids has an intrinsic viscosity of 0.150 when measured as a 2 per cent solution in 1N ammonium chloride at 25°F. The secondary amine analogues can be made by the above process if bis(3-aminopropyl) amine or bis(2-aminoethyl) amine is reacted with urea or thiourea. The piperazine analogues can be made by reacting N,N' - di(3 - aminopropyl) piperazine or N,N' - di(2 - aminoethyl) piperazine

with urea or thiourea. The $-N-C_1$ to C_{22} alkyl analogues can be made by reacting C_1 to C_{22} alkyl bis(3-aminopropyl) amine or C_1 to

C_{22} alkyl bis(2-aminoethyl) amine with urea or thiourea. Additional analogues can be prepared by the following reactions:



The preparation of the other suitable analogues is within the skill of the art following the above techniques.

- 10 The antimicrobial effectiveness of the APU resins was determined using the "Test Tube Serial Dilution Method" described on pages 195-200 of the Fifth Edition of "Diagnostic Bacteriology" by Schaub et al. Table I sets forth the "minimum inhibitory concentration" (MIC) against Streptococcus A and Streptococcus B, two predominant microorganisms isolated from the saliva of a human who is
- 15 subject to calculus formation and caries formation, of an APU resin (Resin A) having an average molecular weight of about 4300 and a repeating unit



- 25 The test composition was 0.5% solution of Resin A in an aqueous alcoholic medium con-

taining 50% by weight of ethanol. Test results are shown in Table I.

TABLE I

Microorganism	MIC in micrograms per millilitre ($\mu\text{g}/\text{ml}$)	30
Streptococcus A	12.8	
Streptococcus B	6.4	

The foregoing results illustrate the highly desirable, unexpected antimicrobial properties of APU resins orally. The antimicrobial properties of APU resins in this test are equivalent to the results obtained with chlorothymol, an effective antimicrobial against the same microorganisms.

Table II sets forth the "minimum inhibitory concentration" (MIC) of Resin A against *Staph aureus* and *P. ovale* as determined using the aforementioned method. Values for well known microbial materials are included for purposes of comparison.

TABLE II

Test Composition	MIC in micrograms per millilitre ($\mu\text{g/ml}$)	
	<i>Staph. aureus</i>	<i>P. ovale</i>
1% Resin A in water	15.6	3.9
1% Resin A in ethanol	—	1.9
1% bis (3,5,6-trichloro-2-hydroxy-phenyl) methane in ethanol	0.5	500
1% 3,4,4' trichlorocarbanilide in ethanol	0.1	500

The antimicrobial properties are surprising in view of the fact that these properties of APU resins were unknown. In addition, effectiveness against *P. ovale* is not generally characteristic of other agents known to be effective against *Staph. aureus*.

MIC results against *P. ovale* for 1% aqueous solutions of other listed APU resins are set forth in Table III.

TABLE III

Polymer		
Repeating Unit	Molecular weight	MIC ($\mu\text{g/ml}$)
$\left[\begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \quad \\ (\text{CH}_2)_3 \text{N} \quad \text{N} (\text{CH}_2)_3 \\ \quad \quad \\ \text{CH}_2 - \text{CH}_2 \end{array} \text{NHC(O)NH} \right]$	5,700	3.9
$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_3 \text{N}^+ - (\text{CH}_2)_3 \text{NHC(O)NH} \\ \quad \quad \\ \text{CH}_2 \quad \text{CHCH}_2 \text{Cl} \\ \\ \text{OH} \end{array} \right]$	6,700	15.6
$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_3 \text{N}^+ - (\text{CH}_2)_3 \text{NHC(O)NH} \\ \quad \quad \\ \text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \\ \quad \quad \diagup \quad \diagdown \\ \quad \quad \text{O} \end{array} \right]$	5,700	15.6

TABLE III (Continued)

Repeating Unit	Molecular weight	MIC (µg/ml)
$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_3 \text{N}^+ - (\text{CH}_2)_3 \text{NHC(O)NH} \\ \\ \text{CH}_2 \text{CHCH}_2\text{OH} \\ \\ \text{OH} \end{array} \right]$	6,200	15.6
$\left[\begin{array}{c} \text{CH}_3 \\ \\ (\text{CH}_2)_3 \text{N}^+ - (\text{CH}_2)_3 \text{NHC(O)NH} \\ \\ \text{CH}_3 \end{array} \right]$	4,700	4.8

5 The same testing technique was employed to determine antimicrobial effectiveness of APU resins in the presence of water-soluble organic detergents and such tests confirm that APU resins exhibit antimicrobial effectiveness against *P. ovale* in the presence of detergents.

10 In addition to their antimicrobial effectiveness, the APU resins have been found to be substantive to proteinaceous substrates, such as hair and skin, and to be effective in inhibiting formation of calculus and caries in the oral cavity.

15 Substantivity was determined by stirring a half-inch diameter circular gelatin disk weighing about 40 milligrams in 10 grams of 1% by weight of radioactive (C-14 tagged) APU resin, rinsing the disk five times in 10 millilitres of water and measuring the radioactive emission with the aid of a radiation detector. 20 These tests showed the APU resin to be significantly more substantive than the well-known antimicrobial compounds listed in Table II. Further, similar tests show that the 25 APU resins retain their substantivity even in the presence of water-soluble synthetic organic detergents. This property is quite surprising because generally antimicrobial effectiveness tends to be destroyed or seriously impaired 30 because of the adverse effect of detergents on substantivity. When a tress of hair weighing 0.55 grams was substituted for the gelatin disk

in the foregoing test, similar substantivity results were obtained in the presence of detergents.

35 The calculus inhibiting properties of the APU resins are demonstrated using an *in vitro* test wherein artificial calculus deposits are formed. More particularly, when two sterilized glass slides (1.3 cm width and 7.6 cm length) 40 are incubated for 24 hours at 37°C in 5 millilitres of a solution containing a 1% concentration of Zipkin-McClure diet (66.5% cornstarch, 27% whole milk powder, 5% whole dried yeast, 0.5% of a salt mixture containing 44.9% sodium chloride, .048% ferric citrate trihydrate and 0.0035% copper sulphate and 1% cod liver oil) and two drops (0.1 ml) 45 of pooled, paraffin simulated human saliva, deposits form on the glass slide which are similar to oral calculus deposits in comparison as they consist primarily of calcium phosphate. 50 Saliva is generated by having a group of people who chew paraffin wax and pooling the saliva of the group. 55

60 The foregoing test provides a convenient means for evaluating calculus inhibiting properties of various compounds by including 1 millilitre of a specific concentration (0.1 to 1.0%, by weight) of a known compound in the incubates solution and thereafter observing the incubated slides and comparing them with slides incubated in the absence of the test com-

pound. Slides are scored according to the following scale:

+ = deposit occurs

0 = no deposit

5 S = slight deposit as compared with the control deposit

10 When a 0.1% solution of Resin A in water was tested in the foregoing test, no deposit was observed on the slide, thereby indicating that small concentrations of APU resin are effective to inhibit formation of calculus in the oral cavity. Again, by way of comparison, the performance of APU resin in this test was equivalent to that of 0.1% chlorothymol, a particularly effective anti-calculus agent; whereas 0.1% heptyl p-hydroxy benzoate, 1.0% hexamethyl phosphoramidate, 0.1% cationic dimethyl polysiloxane and 0.1% of a cationic polymer ("Reren 205MH") were ineffective in the same test.

20 The LD₅₀ of Resin A has been determined to be 1500 milligrams per kilogram, indicating that the aminopolyureylene resins are non-toxic. Accordingly, these materials are safe for use and formulation in any composition designed for application to the oral cavity provided that such carrier compositions do not contain any ingredients which are toxic or would inactivate the APU polymer.

30 In view of the foregoing properties, the described APU resins may be incorporated into a compatible, nontoxic vehicle to form compositions which are suitable for improving the condition of the hair, skin and oral cavity. For example, due to their antimicrobial and substantivity characteristics, the APU resins may be incorporated into a compatible, nontoxic, cosmetic vehicle to form cosmetic compositions for application to the hair and skin. On the other hand, the APU resins may be incorporated into a compatible, nontoxic vehicle to form oral compositions which are effective to improve oral hygiene.

45 The resultant cosmetic compositions of the present invention may be prepared in a wide variety of physical forms. They may be liquids, pastes or solids and may consist of a single aqueous or aqueous-alcoholic phase, or may comprise an aqueous and a separate oily phase as in two-layer systems or emulsions of the water-in-oil or oil-in-water types. By suitable selection of the compatible nontoxic cosmetic vehicle, it is contemplated that the present cosmetic compositions may be prepared in the form of daily skin or hair conditioning products such as skin lotions or hair conditioning rinses, daily hair-grooming products, such as hair lotions, hair dressings or hair tonic, or they may be prepared in the form of cleansing products, such as hair shampoos. Alternatively, the resins may be incorporated into a compatible, nontoxic vehicle to form oral compositions including toothpaste, toothpowder, mouthwash,

65 dental tablets, lozenges, dental floss and chewing gum.

The APU resins will constitute generally a minor proportion, at least 0.05 per cent and usually 0.10 per cent to 10 per cent, by weight of the compositions. However, the proportion will vary depending on the nature of the product. For example, concentrations in the range of 0.25 per cent to 10 per cent, more usually 0.5 per cent to 3.0 per cent, by weight, are preferred for hair and skin conditioning products and hair grooming compositions; whereas, concentrations of resin the range of 1 per cent to 10 per cent, preferably 1 per cent to 5 per cent, by weight, are preferred for solid and liquid cleansing compositions. On the other hand, the usual preferred concentrations in oral compositions will be in the range 0.05 per cent to 3 per cent by weight and effective to inhibit growth of oral streptococcal microorganisms and to inhibit formulation of calculus.

The vehicle accounts for the balance, generally 90 per cent to 99.9 per cent by weight, of the cosmetic skin and hair compositions, and its specific composition will vary according to the end use of the composition. Thus the vehicle in single-phase, liquid, hair- or skin-conditioning compositions may be a C₂-C₃ lower monohydric or polyhydric alcohol or a mixture thereof; for example, the composition may contain 1% to 15% by weight of a C₂-C₃ monohydric alcohol. Where a liquid hair-grooming composition results, the vehicle will generally contain from 0.5 per cent to 65 per cent by weight of a non-volatile hair-grooming agent and from 25 to 99.4 per cent by weight of aqueous solvent, such as a mixture of water and ethanol or isopropyl alcohol. In liquid cleansing compositions, such as shampoos, the vehicle will generally contain 5 to 40 per cent, preferably 10 to 30 per cent, by weight of a compatible, water-soluble synthetic organic detergent. On the other hand, in solid, powder, or cream cleansing compositions the vehicle will generally contain from 15 to 99 per cent by weight of the organic detergent and the balance water and/or other components. The proportions of all vehicle components are expressed as per cent by weight of the total composition.

In the case of cleansing compositions for the hair and skin, such as shampoo, the vehicle includes a cleansing agent which is a water-soluble synthetic organic detergent. Suitable detergents may be selected from anionic, nonionic, amphoteric, zwitterionic, polar nonionic and cationic detergents, and mixtures of two or more of these detergents. In preferred liquid shampoo compositions which are characterised by copious foam, cosmetic conditioning and effectiveness in inhibiting formation of visible masses of epidermal cellular debris harbouring *P. ovale*, 0.5 per cent by weight of amino-polyureylene resin is

generally included in an aqueous detergent mixture which consists essentially of from 10% to 30% by weight of a betaine detergent, 1% to 10% by weight of a water-soluble anionic sulphate, anionic 2 hydroxyalkyl detergent, amine oxide or amphoteric detergent, and 1% to 10% by weight of a water-soluble nonionic detergent containing polyoxypropylene groups and polyoxyethylene groups. The detergent weights are based upon the total weight of the shampoo.

The compatible anionic surface active agents include those surface active detergent compounds which contain an organic hydrophobic group, generally having 8 to 26 carbon atoms and preferably 10 to 18 carbon atoms, in their molecular structure, and at least one water-solubilizing group selected from sulphonate, sulphate, carboxylate, phosphonates and phosphate so as to form a water-soluble detergent.

Examples of suitable anionic detergents are water-soluble salts, e.g. the sodium, ammonium and alkylolammonium salts, of higher fatty acids or resin acids containing 8 to 20 carbon atoms, preferably 10 to 18 carbon atoms. Suitable fatty acids can be obtained from oils and waxes of animal or vegetable origin, e.g. tallow, grease, coconut oil, tall oil and mixtures thereof. Particularly useful are the sodium and potassium salts of the fatty acid mixtures derived from coconut oil and tallow, e.g. sodium coconut soap and potassium tallow soap.

The anionic class of detergents also includes water-soluble sulphated and sulphonated synthetic detergents having an alkyl radical of 8 to 26, preferably 12 to 22, carbon atoms in their molecular structure. The term "alkyl" includes the alkyl portion of the higher acyl radicals.

Examples of sulphonated anionic detergents are higher alkyl mononuclear aromatic sulphonates such as higher alkyl benzene sulphonates containing from 10 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, e.g. the sodium, potassium and ammonium salts of higher alkyl benzene sulphonates, higher alkyl toluene sulphonates, higher alkyl phenol sulphonates and higher naphthalene sulphonates. A preferred sulphonate is a linear alkyl benzene sulphonate having a high content of 3- (or higher) phenyl isomers and a correspondingly low content (well below 50 per cent) of 2- (or lower) phenyl isomers, i.e. wherein the benzene ring is preferably attached in large part at the 3 or higher (e.g. 4, 5, 6 or 7) position of the alkyl group and the content of isomers in which the benzene ring is attached at the 2 or 1 position is correspondingly low.

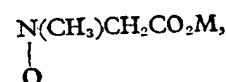
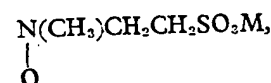
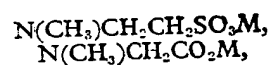
Other suitable anionic detergents are olefin sulphonates, including long-chain alkene sulphonates, long-chain hydroxy-alkane sulphonates and mixtures of alkene sulphonates and hydroxy-alkane sulphonates. These olefin sul-

phonate detergents may be prepared in a known manner by the reaction of sulphur trioxide with long-chain olefins containing 8 to 25, preferably 12 to 21, carbon atoms and having the formula $RCH=CHR_1$ where R is a higher alkyl group of 6 to 23 carbons and R_1 is an alkyl group of 1 to 17 carbons or hydrogen to form a mixture of sultones and alkene sulphonic acids which is then treated to convert the sultones to sulphonates.

Other examples of sulphate or sulphonate detergents are paraffin sulphonates containing 10 to 20, preferably 15 to 20, carbon atoms, e.g. primary paraffin sulphonates made by reacting long-chain alpha olefins and bisulphites, and paraffin sulphonates having the sulphonate groups distributed along the paraffin chain; sodium and potassium sulphates of higher alcohols containing 8 to 18 carbon atoms such as sodium lauryl sulphate and sodium tallow alcohol sulphate; sodium and potassium salts of α -sulphofatty acid esters containing 10 to 20 carbon atoms in the acyl group, e.g. methyl α -sulphomyristate and methyl α -sulphotallowate; ammonium sulphate of mono- or diglycerides of higher (C_{10} - C_{18}) fatty acids, e.g. stearic monoglyceride monosulphate; sodium and alkylolammonium salts of alkyl polyethenoxy ether sulphonates produced by condensing 1 to 5 moles of ethylene oxide with one mole of higher (C_8 - C_{18}) alcohol; sodium higher alkyl (C_{10} - C_{18}) glyceryl ether sulphonates; and sodium or potassium alkyl phenol polyethenoxy ether sulphonates with 1 to 6 oxyethylene groups per molecule and in which the alkyl radicals contain 8 to 12 carbon atoms.

The suitable anionic detergents include also C_8 - C_{18} acyl sarcosinates (e.g. sodium lauroyl sarcosinate), sodium and potassium salts of the reaction product of higher fatty acids containing 8 to 18 carbon atoms in the molecule esterified with isethionic acid, and sodium and potassium salts of the C_8 - C_{18} acyl N-methyl taurides, e.g. sodium cocyl methyl taurate and potassium stearyl methyl taurate.

Other suitable anionic detergents are N-(2-hydroxy C_{10} - C_{18} alkyl) derivatives of N-methyl taurinate, sarcosinate, N-methyl taurinate-N-oxide, sarcosinate-N-oxide and diethanolamine. These detergents correspond to the formula R_1X wherein R_1 is a 2-hydroxy alkyl group containing 10 to 18 carbon atoms and X is selected from



and



wherein

M is selected from sodium, potassium, ammonium and mono, di and triethanol-ammonium.

The N-(2-hydroxy higher alkyl) N-methyl taurinates have the formula



and may be prepared by simple addition of N-methyl taurine salt to a 1,2 epoxy-alkane containing about 10 to 18 carbon atoms. The addition technique produces an N-(2-hydroxy-alkyl) N-methyltaurine salt which is relatively free from inorganic impurities. The epoxide raw material is made by conventional oxidation of compounds derived from petroleum. The N-oxide derivatives of the N-(2-hydroxy-alkyl) N-methyl taurinates may be prepared by oxidizing the corresponding N-(2-hydroxyalkyl) N-methyl taurinate with hydrogen peroxide or ozone to convert the amine to an amine oxide. The N-(2-hydroxyalkyl) sarcosinates, $RCH(OH)CH_2N(CH_3)CH_2CO_2M$, and their N-oxides may be prepared in the same manner as the taurinate derivatives. The N-(2-hydroxy-alkyl) diethanolamine is similarly prepared by adding diethanolamine to the desired 1,2-epoxyalkane.

Anionic phosphate surfactants in which the anionic solubilizing group attached to the hydrophobic group is an oxyacid of phosphorus are also useful in the detergent compositions. Suitable phosphate surfactants are sodium, potassium and ammonium alkyl phosphate esters such as $(R-O)_2PO_2M$ and $ROPO_2M$ in which R represents an alkyl chain containing from 8 to 20 carbon atoms or an alkyl phenyl group containing 8 to 20 carbon atoms and M represents a soluble cation. The compounds formed by including one to 40 moles of ethylene oxide in the foregoing esters, e.g. $[R-O(EtO)_n]_2PO_2M$, are also satisfactory.

The particular anionic detergent salt will be suitably selected depending upon the particular formulation. Suitable salts include the ammonium, substituted ammonium (mono-, di and triethanolammonium), alkali metal (such as sodium and potassium) and alkaline earth metal (such as calcium and magnesium) salts. Preferred salts are the ammonium, triethanol-ammonium, sodium and potassium salts of higher alkyl sulphates and C_8-C_{18} acyl sarcosinates.

The nonionic synthetic organic detergents are generally condensation products of an organic aliphatic or alkyl aromatic hydrophobic compound and hydrophilic ethylene oxide groups. Practically any hydrophobic compound having a carboxy, hydroxy, amido, or amino group with a free hydrogen attached to the nitrogen can be condensed with ethylene oxide or with the polyhydration product thereof, polyethylene glycol, to form a nonionic deter-

gent. Further, the length of the polychenocoxy chain can be adjusted to achieve the desired balance between the hydrophobic and hydrophilic elements.

The nonionic detergents include the polyethylene oxide condensate of one mole of an alkyl phenol containing from 6 to 12 carbon atoms in a straight- or branched-chain configuration with 5 to 30 moles of ethylene oxide, e.g. nonyl phenol condensed with 9 moles of ethylene oxide, dodecyl phenol condensed with 15 moles of ethylene oxide and dinonyl phenol condensed with 15 moles of ethylene oxide. Condensation products of the corresponding alkyl thiophenols with 5 to 30 moles of ethylene oxide are also suitable.

Still other suitable nonionics are water-soluble polyoxyethylene and polyoxypropylene adducts of C_1-C_8 alkanols which are sold under the trade mark 'UCON'. These nonionics have a molecular weight in the range of about 600 to about 4,000 and consist of a heteric chain of oxyethylene and oxypropylene condensed on a C_1-C_8 alkanol. The weight ratio of oxyethylene to oxypropylene may be in the range from 3:1 to 1:3. A preferred nonionic detergent of this type is "Ucon 50HB 5100", which has a molecular weight of about 4,000 and is the condensation product of a mixture of 50% ethylene oxide and 50% propylene oxide on butanol.

Also included in the nonionic detergent class are condensation products of a higher alcohol containing 8 to 18 carbon atoms in a straight or branched-chain configuration condensed with 5 to 30 moles of ethylene oxide, e.g. lauryl-myristyl alcohol condensed with 16 moles of ethylene oxide.

A particularly useful group of nonionics is marketed under the trade mark 'PLURONIC'. The compounds are formed by condensing ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The molecular weight of the hydrophobic portion of the molecule is generally in the range 950 to 4,000 preferably 1200 to 3500. The addition of polyoxyethylene radicals to the hydrophobic portion tends to increase the solubility of the molecule as a whole. The molecular weight of the block copolymers varies from 1300 to 15,000 and the polyethylene oxide content may be 10 to 80 per cent by weight. "Pluronic L-62" having a hydrophobe molecular weight of 1,750 and containing 20% by weight of ethylene oxide is a preferred nonionic detergent.

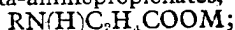
Other suitable nonionics may be derived by the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine. The molecular weight varies from 500 to 4,500.

Other nonionic detergents include ethylene oxide addends of monoesters of hexahydric alcohols and inner ethers thereof with higher

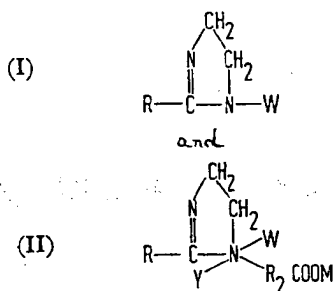
fatty acids containing 10 to 20 carbon atoms, e.g. sorbitan monolaurate, sorbitan monooleate and mannitan monopalmitate.

- 5 The amphoteric detergents which can be used in the compositions of this invention are generally water-soluble salts of derivatives of aliphatic amines which contain at least one cationic group, e.g. non-quaternary nitrogen, quaternary ammonium or quaternary phosphonium group, at least one alkyl group of 8 to 18 carbon atoms and an anionic water-solubilizing carboxyl, sulphy, or sulphato group in their molecular structure. The alkyl group may be straight chain or branched and the specific cationic atom may be part of a heterocyclic ring.

Examples of suitable ampholytic detergents are alkyl beta-aminopropionates,



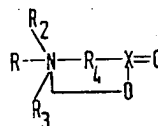
- 20 alkyl beta-iminodipropionates,
 $\text{RN}(\text{C}_2\text{H}_4\text{COOM})_2;$
 alkyl and hydroxy alkyl taurinates,
 $\text{RN}(\text{CH}_2)_n\text{SO}_3\text{M};$
 and long-chain imidazole derivatives having
 25 the following formulae:



- wherein R is an acyclic group of 7 to 17 carbon atoms; W is selected from R_2OH , R_2COOM , and $\text{R}_2\text{OR}_2\text{COOM}$; Y is OH^- or R_2OSO_3^- ; R_2 is an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms; R_3 is selected from alkyl, alkyl aryl and fatty acyl glyceride groups having 6 to 18 carbon atoms in the alkyl or acyl group; and M is a water-soluble cation, e.g. sodium potassium, ammonium or alkylolammonium.

- Formula I detergents are disclosed in Volume II of "Surface Active Agents and Detergents" and Formula II detergents are described in issued patents. The acyclic groups may be derived from coconut oil fatty acids (a mixture of fatty acids containing 8 to 18 carbon atoms), lauric fatty acid or oleic fatty acid, and the preferred groups are C_8 — C_{17} alkyl groups. Preferred detergents are sodium N-lauryl beta-aminopropionate, disodium N-lauryl iminodipropionate, and the disodium salt of 2-lauryl-cycloimidium-1-hydroxyl, 1-ethoxyethanoic acid or 1-ethanoic acid.

Zwitterionic detergents having the following formula are also useful:



wherein R is a radical selected from C_{10} — C_{16} alkyl, C_{10} — C_{16} alkyl amidoethyl and C_{10} — C_{16} alkyl amidopropyl; R_2 and R_3 are each C_1 — C_3 alkyl or C_1 — C_3 hydroxyalkyl; R_4 is an alkylene or hydroxyalkylene group containing 1 to 4 carbon atoms; and X is C or S:O. When R_4 is CH_2 and X is C, the detergent is called a betaine; and when R_4 is CH_2 and X is S:O, the detergent is called a sulphobetaine or sultaine. Examples of betaine and sulphobetaine detergents are 1-(lauryl dimethylammonio) acetate, 1-(myristyl dimethylammonio)propane - 3 - sulphonate and 1-(myristyl - dimethylammonio) - 2 - hydroxypropane-3-sulphonate. Preferred detergents are the coconut-oil derived alkyl dimethyl betaine and the alkyl amidopropyl dimethyl betaine detergents in which the alkyl group contains 3% C_8 , 7% C_{10} , 48% C_{12} , 18% C_{14} , 9% C_{16} , and 10% C_{18} .

The polar nonionic detergents are those in which the hydrophilic group contains a semi-polar bond directly between two atoms, for example, N—O; P—O, As—O or S—O. There is charge separation between the two directly bonded atoms, but the detergent molecule bears no net charge and does not dissociate into ions.

The polar nonionic detergents useful in this invention include open-chain aliphatic amine oxides of the general formula $\text{R}_1\text{R}_2\text{R}_3\text{N—O}$. For the purposes of this invention R_1 is an alkyl, alkenyl or monohydroxyalkyl radical having from 10 to 16 carbon atoms. R_2 and R_3 are each selected from methyl, ethyl, propyl, ethanol and propanol radicals.

Other operable polar nonionic detergents are the open-chain aliphatic phosphine oxides having the general formula $\text{R}_1\text{R}_2\text{R}_3\text{P—O}$ wherein R_1 is an alkyl, alkenyl or monohydroxyalkyl radical ranging in chain length from 10 to 18 carbon atoms, and R_2 and R_3 are each alkyl or monohydroxyalkyl radicals containing from 1 to 3 carbon atoms.

The cationic detergents contain an organic hydrophobic group and a cationic solubilizing group. Typical cationic solubilizing groups are amine and quaternary groups.

Examples of suitable cationic detergents are normal primary amines RNH_2 , wherein R is C_{12} — C_{15} ; diamines such as those of the type $\text{RNHC}_2\text{H}_4\text{NH}_2$, wherein R is an alkyl group of 12 to 22 carbon atoms, such as N-2-aminoethyl stearyl amine and N-2-aminoethyl myristyl amine; amide-linked amines such as

- hair-grooming agent to facilitate grooming of the hair and scalp and to keep the hair in place. Examples of such agents are castor oil, mineral oil; lipophilic lower alkoxypolypropylene glycols having a molecular weight greater than 1000, e.g. in the range of 1,000 to 2,500, such as butoxy polyoxypropylene glycols having a molecular weight of about 1,700; hydrophobic mixed polyethylene polyalkylene (C_3-C_{14}) glycols having a molecular weight of about 400 to 4,000 and containing from 35 to 65 per cent by weight of polyethylene glycol, on butanol, such as "Ucon 50 HB 660"; polyhydric alcohols containing 2 or 3 carbon atoms such as glycerol and propylene glycol; C_1-C_3 alkyl and hydroxyalkyl esters of C_8-C_{18} fatty acids; and gums, such as gum tragacanth. It is preferred to employ those substantially non-volatile organic grooming agents which have a molecular weight of above 75, and preferably above 200, and which contain an alcoholic hydroxy group, such as the aforementioned glycols, polyhydric alcohols, polymerized alkylene oxides and castor oil.
- The concentration of the non-volatile, organic hair-grooming agent in the hair-grooming compositions will generally be in the range from 0.5 to 65 per cent, preferably from 3 to 50 per cent, e.g. from 3 to 30 per cent, by weight of the composition. The balance of the vehicle will vary according to the form of the resultant product, and generally will be an aqueous medium, such as water or a mixture of water and a lower monohydric alcohol, such as ethanol or isopropanol. In the aqueous alcoholic mixtures, as little as 5 per cent by weight of water may be present with the balance being lower alcohol. Single-phase compositions may include 30 per cent to 80 per cent by weight of water, whereas emulsion compositions generally will be free of alcohol.
- The cosmetic compositions for the hair and skin may also contain as adjuvant materials various substances, such as vitamins, lanolin, bacteriocides, plant extracts, colouring agents, perfumes, thickeners such as cellulose, opacifiers and sequestering agents in order to enhance the cosmetic or antimicrobial properties of the resultant compositions. Buffers may also be included to provide a pH of 5 to 10, and preferably from 7.0 to 9.0.
- The hair and skin compositions of the invention are characterised by an outstanding ability to inhibit the growth of *P. ovale*, the yeast believed to be associated with dandruff. These compositions are also substantive (remain on the hair and skin) and thereby retain bacteriostatic effectiveness over an extended period of time. In clinical testing, cleansing compositions have proven effective in controlling the formation of dry, flaky scales of sloughed-off skin. Further, the compositions effectively condition the hair and skin and, depending upon their nature, are effective as hair

grooming compositions or cleansing compositions. 65

Specific skin and hair compositions, according to the invention, are illustrated by the following Examples. All quantities indicated are by weight unless otherwise indicated. 70

Example 1.

A cleansing composition suitable for use as a shampoo.

	Percent	
$C_{10}-C_{16}$ alkyl *amidopropyl dimethyl betaine	16.0	75
Triethanolamine lauryl sulphate	4.0	
Lauryl dimethyl amine oxide	0.5	
Polyoxypropylene - polyoxyethylene block copolymer having a hydrophobic molecular weight of 1,750 and containing 20% by weight of polyoxyethylene	5.0	80
Condensation of product of a 1:1 mixture of ethylene oxide and propylene oxide on butanol (m.w. = 4000)	2.0	85
Resinous condensate of about 2 moles of epichlorohydrin and one mole of diethylene-triamine having a molecular weight of about 80,000	0.5	90
Resin A	2.0	
Ethanol	1.9	
Water	balance	95
	100.0	

*Alkyl group corresponds to the mixture of alkyls obtained from a middle-cut of coconut oil, e.g., 1% C_{10} , 65% C_{12} , 27% C_{14} , and 7% C_{16} . 100

The foregoing composition is prepared by admixing the surfactant ingredients with the formula weight of water with agitation at a temperature in the range of 130°F. to 160°F. Resin A and the resinous condensate ingredients are added to the aqueous surfactant mixture with agitation at a temperature in the range of 145°F. to 160°F. After homogeneity is attained, the mixture is cooled to 80°F.—90°F. with agitation and the pH is adjusted, if necessary, by adding either sulphuric, hydrochloric or citric acid, or triethanolamine, sodium hydroxide or potassium hydroxide. The resultant product is a clear liquid at pH 7.5 and has a cloud point below 32°F. The shampoo exhibits outstanding cleaning, foaming, and hair-conditioning properties in normal shampooing operations. 105

The outstanding foaming characteristics of the shampoo of Example 1 in the presence of sebum soil are illustrated by the following test. Twenty-five grams of shampoo solution are diluted to 100 ml with water containing 250 parts per million of hardness (160 ppm. of 110 115 120

Ca⁺⁺ and 90 ppm. of Mg⁺⁺) in the presence of three grams of synthetic sebum soil, and the temperature of the mixture is adjusted to 100°F. The 100 ml of solution is then transferred to a 500 ml graduated cylinder (total volume capacity of over 600 ml of water) containing a water-filled plastic cylinder (17 mm diameter, 72 mm high and displacement volume equal to 25 ml of water), and the 500 ml cylinder is affixed to a mechanical rotator where by it is rotated through 20 complete revolutions to generate foam. Rotations are completed within 35 to 55 seconds. The foam volume is noted at the conclusion of the rotations, and the time interval in seconds from the completion of the rotations to the point at which 75 ml of liquid have been drained is recorded as the drainage time. The values for the composition of Example 1 are 650 cc of total foam and 300 seconds foam-drainage time. Comparable figures for high-foaming, high performing, commercial shampoos based on alkyl sulphate detergent are 475 cc foam volume and 139 seconds foam drainage time.

Resin A has a beneficial effect upon foam volume and foam stability because comparable figures for a composition not containing APU resin are 450 cc of foam and 100 seconds foam drainage time.

When the antimicrobial effectiveness of the foregoing composition against *P. ovale* is determined using the "Test Tube Serial Dilution Method" the composition exhibits a "minimum inhibitory concentration" (MIC) of 98 µg/ml based on the weight of shampoo or 1.95 µg/ml based upon the weight of the APU resin. Further, when the composition is formulated with a radioactive C₁₄ tagged Resin A and checked for protein substantivity, a value of 414 µg/ml per disk is noted. Substantivity is determined by stirring a half-inch diameter circular gelatin disk weighing 42 mg for 15 minutes in ten grams of a 25% weight concentration of shampoo containing radioactive (C₁₄ tagged) APU Resin A, rinsing the disk five times in 10 ml of water, and measuring the radiation emission with the aid of a thin window gas flow Geiger-Müller counter.

The antidandruff properties of the sham-

poo composition were determined in clinical testing wherein the composition of Example 1 was compared with a 17% by weight triethanolamine myristate placebo shampoo composition known to be ineffective against dandruff and a commercial antidandruff shampoo containing the zinc pyridinethione as the antidandruff ingredient. In the clinical test, a skilled evaluator determined dandruff rating for each of the subjects before beginning testing, once a week during the two weeks on the placebo shampoo (to establish a baseline), and once a week during the six weeks on the test shampoo. For one third of the group, the placebo shampoo was the test shampoo. During the six week test period, each subject washed his hair with 18 cc of shampoo using half of the shampoo in each of the two consecutive washings, had his dandruff rating determined on the seventh day, and shampooed again after the rating. Between shampoos, each subject used only a specified hairdressing having minimum effect on dandruff scores. The test results indicated that the composition of Example 1 was effective in reducing dandruff, and its effectiveness was equivalent to that of the commercial shampoo containing zinc pyridinethione.

During testing, the cosmetic conditioning characteristics of the composition of Example 1 were evaluated against commercial shampoo formulations by skilled beauty operators using the well known "half head" technique. The composition of the example showed a marked advantage in wet and dry combing, and was equivalent in curl-retention and static-charge reduction.

Examples 2 and 3.

The composition of Example 1 is repeated with the exception that the concentration of triethanolamine lauryl sulphate (TEALS) is reduced from 4% by weight to 2% and 1% by weight. The resultant products are clear, homogeneous shampoos having cosmetic conditioning properties comparable to those of Example 1. The foaming characteristics in the presence of sebum soil are determined using the method outlined in Example 1 with the following results.

Example	Foam Volume (cc)	Drainage Time (sec.)
2 2% TEALS	650	154
3 1% TEALS	550	138

These results show that a reduction in the supplementary detergent, TEALS, may result

in a reduction in both foam volume and foam stability.

Examples 4-6.

5 The composition of Example 1 is repeated with the exception that 4% by weight of the disodium salt of 2 undecyl, 1-ethoxyethanoic acid, 1 ethanoic acid, 1-lauryl sulphate imidazoline sold as "Miranol 2 MCA", sodium N-lauryl sarcosinate, and a mixture of sodium N-lauryl myristyl-aminopropionate (9 parts)

and disodium N-lauryl myristyl iminodiprionate (1 part) sold as "Deriphat 170C" (DERIPHAT is a trade mark) respectively is substituted for the 4% of the triethanolamine sulphate detergent. Foaming results using the test method in Example 1 are tabulated in Table IV. 10 15

TABLE IV

Example	Detergent	Foam Volume (cc)	Foam Stability (cc)
4	"Miranol 2MCA"	600	157
5	Sodium N-lauroyl sarcosinate	650	150
6	"Deriphat 170"	650	98

20 The resultant shampoos have satisfactory foaming properties and exhibit cosmetic conditioning properties when used in shampooing. Antimicrobial effects against *P. ovale* are comparable to those of Example 1.

When sodium N(2-hydroxyhexadecyl) N-methyl taurinate or sarcosinate or their N-

oxides are substituted for triethanolamine sulphate detergent in the composition of Example 1, satisfactory "complete" shampoos are also achieved. 25

Example 7.

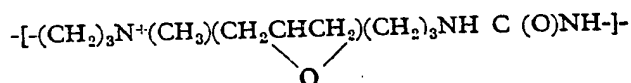
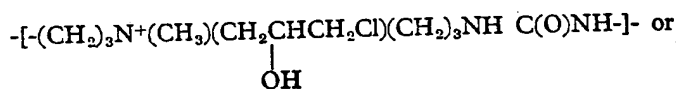
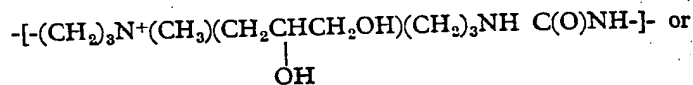
A shampoo having the following composition is prepared. 30

	Percent
Coconut alkyl amidopropyl dimethyl betaine*	16.0
Triethanolamine lauryl sulphate	1.0
"Pluronic L-62"	5.0
Analogue of Resin A having repeating unit	
$-\text{[-(CH}_2\text{)}_3\text{N}^+(\text{CH}_2)_3\text{(CH}_2\text{)}_3\text{NH C(O)NH-]}-$	1.0
a molecular weight of about 4600	balance
Water	
	100.0

*Alkyl mixture derived from middle-cut of coconut oil.

45 The resultant antidandruff shampoo is a clear liquid which exhibits good foaming and conditioning properties when used in shampooing.

When resins having an average molecular weight in the range of 1,000 to 20,000 and a repeating unit of 50

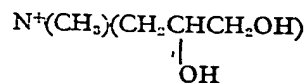


55 are substituted for the resin in the composition of Example 7, substantially similar results are obtained.

Example 8.

The composition of Example 1 is repeated but 1% by weight of the N,N'-di(3-amino-propyl) piperazine urea resin having a molecular weight of about 5600 is substituted for Resin A. The resultant clear liquid shampoo exhibits antimicrobial effectiveness against *P. ovale* and good conditioning effects as evidenced by low static and easy wet and dry combing.

or



in the repeating group are substituted for Resin A in the composition of Example 9.

Example 10.

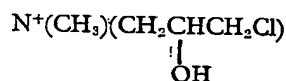
A satisfactory shampoo having the following composition is prepared.

Example 9.
The following clear antidandruff shampoo composition is prepared.

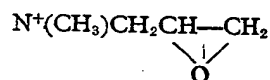
	Weight percent
15 Coconut alkyl amidopropyl dimethyl betaine*	22.5
Sodium N - (2 - hydroxy hexadecyl) N - methyl taurinate	6.0
20 Sodium hexyl benzene sulfonate	0.8
C ₁₂ -C ₁₆ alkyl dimethyl amine oxide	0.6
25 Polyoxypropylene - polyoxyethylene block copolymer (hydrophobe molecular weight of 1750 and 20% by weight of polyoxyethylene)	5.0
30 Resin A	2.0
Water	balance
	100.0

*Alkyl mixture derived from middle-cut of coconut oil.

35 Similar results may be obtained when the quaternized analogues of Resin A containing



or



% By Weight

Coco-dimethyl amidopropyl glycine*	16.0	
Lauryl-bishydroxyethyl amine oxide	4.0	50
Condensation product of 1:1 mixture ethylene oxide and propylene oxide on butanol (M.W. = 4000)	2.0	55
Polyoxypropylene - polyoxyethylene block copolymer having a hydrophobic molecular weight of 1750 and containing 20% by weight of polyoxyethylene	5.0	60
Quaternary ammonium substituted cellulose ether polymer obtained from Union Carbide (U.S.A.) under the name "JR-IL" (a)	2.5	65
Resin A	2.0	
Ethanol	1.9	
Water	balance	70
	100.0	

*Alkyl mixture derived from middle-cut of coconut oil.

(a) Molecular weight in range of 100,000 to 1,000,000.

The pH of the foregoing shampoo is adjusted to 7.5 with 10% hydrochloric acid solution. This shampoo exhibits good foam volume and high foam stability when tested using the procedure used with Example 1.

Examples 11-14 describe additional cleansing compositions suitable for use as shampoos.

Ingredient	Examples			
	11	12	13	14
Weight %				
Sodium lauryl sulphate	—	—	10.0	—
Triethanolamine lauryl sulphate	—	12.0	—	—
Sodium lauryl ether sulphate	8.0	—	—	—
C ₈ —C ₁₈ alkyl dimethyl betaine	—	—	10.0	—
Triethanolamine lauryl-myristyl amino propionate	—	—	—	4.2
Disodium salt of 2-undecyl cycloimidium, 1-hydroxy, 1-ethoxyethanoic acid, 1-ethanoic acid	—	6.0	—	—
Lauryl dimethyl amine oxide	7.5	—	—	8.1
Cetyl dimethyl amine oxide	—	—	—	2.7
Dimethyl tallow alkyl amidopropyl ammonium chloride	—	—	—	2.7
Lauric myristic diethanolamide	—	—	—	2.1
Resin A	1.0	1.0	1.0	1.0
Ethanol	10.0	10.0	10.0	—
Water	bal.	bal.	bal.	bal.
	100.0	100.0	100.0	100.0
pH	9.3	8.0	9.0	9.2

The foregoing compositions are effective to inhibit growth of microorganisms such as *P. ovale* and exhibit desired cosmetic properties.

- 5 Example 15 sets forth a cleansing composition suitable for use as a shampoo, and Examples 16—19 set forth other suitable cleansing compositions. All of these compositions are prepared by adding an aqueous solution containing 40.2% by weight of Resin A to the aqueous mixture of the other ingredients with agitation at 78°F. The pH of compositions 17 and 18 is adjusted to 7.2 using 10% aqueous hydrochloric acid. The unadjusted pH of Example 19 is 7.2.

Example 15.

	Per cent by weight	
Sodium lauryl sulphate	27.0	20
Linear hexylbenzene sulphonate	1.0	
Resin A	1.0	
Water	Balance	
	100.0	
MIC of composition = 0.49 µg/ml. (based upon the resin).		25
MIC of composition without APU = 250 µg/ml.		

Examples 16 — 19

	16	17	18	19
C ₈ —C ₁₈ amidopropyl betaine	20			
Lauryl dimethyl amine oxide		20		
Block copolymer of propylene oxide-ethylene oxide (20% by weight) — m:w = 2200			20	
Sodium N-lauryl-myristyl beta-aminopropionate				20
Ethanol	10	10	10	10
Resin A	1	1	1	1
Water	bal.	bal.	bal.	bal.
	100	100	100	100

These compositions are similarly effective and exhibit desired cosmetic properties.

Example 20.

(Detergent Bar)

	Per cent
5 Sodium N, lauryl B iminodipropionate	8.75
Sodium C ₁₀ —C ₂₀ alkane sulphonate	24.25
Sodium tallow soap	26.40
10 Sodium tridecylbenzene sulphonate	7.30
Syrupy phosphoric acid (85%)	7.30
Stearic acid	3.60
Resin A	8.10
15 Water	balance
	100.0

The detergent bar is prepared by admixing 20 parts by weight of 40.2 per cent Resin A solution with 80 parts by weight of a particular mixture of the other ingredients containing about 3 per cent moisture, milling on a three-roll mill and plodding at about 110°F. to yield a rod for cutting into bars. This bar is effective against *Staph. aureus* and *P. ovale* when used for washing hands.

Example 21 sets forth a single-phase hair tonic.

Example 21.

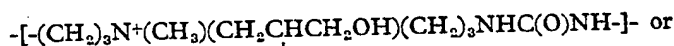
	Per cent	
Ethanol	60.0	30
2,2',4,4' tetrahydroxybenzophenone	0.2	
Polypropoxylated butanol having a mol. wt. of 2500	1.75	
Polypropoxylated butanol having a mol. wt. of 2000	0.5	35
Copolymer of ethylene oxide and propylene oxide on butanol having a molecular weight of 1500 (50% E+O) and 50% PrO)	15.75	40
Perfume	0.5	
1% colour solution	0.1	
Resin A	0.5	
Water	balance	45
	100.00	

Other hair-grooming preparations which are effective against *P. ovale* are set forth in Examples 22—24.

Example 22.
Hair Tonic

Ethyl alcohol 96%	80.0	
Isopropyl myristate	10.0	
Resin A	1.0	
Perfume, colouring	0.4	55
Water	8.6	
	100.0	

	Example 23.		Part II:		
	Hair Cream (Oil-in-water emulsion)		Borax	0.5	30
	Part I:		Resin A	1.5	
	Mineral oil	40.0	Water	44.5	
5	White Petrolatum	5.0	Part III:		
	Stearic Acid	3.0	Perfume	0.3	
	Cetyl Alcohol	1.5			
	Preservative	0.2			
	Part II:		Components of part I are combined by melting together at 75°C. Then part II previously heated to 75°C. is added with stirring at this temperature. The cream is stirred for 10 minutes at 70—75°C. and then cooled slowly with stirring to 45°C. At this temperature part III is added. After cooling with stirring to 30°C. the cream is homogenized.		35
10	Triethanolamine	1.3			
	Resin A	1.0			
	Water	47.7			40
	Part III:				
	Perfume	0.3			
15	Part I is heated to 65°C. and slowly added with thorough stirring to part II previously heated to 60°C. The cream is cooled with stirring to 40°C. at which temperature part III is added.				



are substituted for the resin in the compositions of Examples 15—24, substantially similar results are obtained.

- 60 In the preparation of dentifrice compositions in the form of a paste, powder or tablet, a dentally acceptable water-insoluble polishing agent is usually the major ingredient and is generally present in amounts from 20% to 95% by weight. Usual weight concentrations are 70% to 95% in toothpowders and 20% to 75% in tablets and toothpaste or cream. Representative polishing agents include, for example, dicalcium phosphate, tricalcium phosphate, insoluble sodium metaphosphate, aluminium hydroxide, magnesium carbonate, hydrated silica, calcium sulphate,

bentonite and suitable mixtures thereof. It is preferred to use the water-insoluble calcium or magnesium salts as the polishing agents and, more particularly, calcium carbonate and/or a calcium phosphate, such as dicalcium phosphate dihydrate. In addition to the polishing agent, the dentifrice compositions in powder, tablet and paste form may include from 1% to 3% by weight of a nonionic, cationic or anionic detergent, preferably sodium N-lauroyl sarcosinate, and a sufficient amount of a fluoride containing compound such as sodium monofluorophosphate (Na₂FPO₃), sodium fluoride or stannous fluoride to provide from 0.05% to 0.15%, preferably 0.1%, of fluoride ion in the final product.

75

80

85

In dental cream compositions the polishing agent, APU resin and optional ingredients are proportioned in a liquid medium comprising water and a humectant such as glycerine, propylene glycol or sorbitol solution. The liquid medium amounts to 20% to 75% by weight of the cream. The humectant amounts to 15% to 40% by weight of the dental cream. Such creams preferably include from 0.5% to 10% by weight of a gelling agent such as natural and synthetic gums and gum-like materials, e.g. Irish moss, gum tragacanth, sodium carboxymethylcellulose, polyvinylpyrrolidone or starch.

In addition to the APU resin, polishing agent and optional ingredients discussed above, tablet compositions generally include from 30% to 50% by weight of mannitol, starch or lactose, 2% to 10% by weight of a polyethylene glycol (m.w. of 3000 to 10,000) or polyvinyl pyrrolidone binder and 1% to 2% by weight of a die lubricant such as magnesium stearate, magnesium silicate, sodium benzoate or talc.

Mouth washes or rinses are also within the scope of the invention. Such products generally contain an effective amount of APU resin in the range from 0.05% to 3.0% by weight in a suitably flavoured aqueous alcoholic medium containing from 4% to 70%, preferably 5% to 40%, by weight of a C₂-C₈ alkanol such as ethanol.

Suitable liquid dentifrices are similar to the mouth washes, but also contain minor proportions of 0.5% to 3.0% by weight of a surface active material and from 0 to 30% by weight of a polishing agent such as a particulate aluminium hydroxide. When a polishing agent is present, the liquid will also contain from 2% to 5% by weight of a gelling agent such as sodium carboxy-methylcellulose or an alginate.

In the case of chewing gum, an effective amount of APU resin the range 0.05% to 3% by weight is incorporated in one of the usual warm gum bases. For example, the resin can be incorporated in a warm gum base with stirring to distribute the resin uniformly therein. It can also be added to the exterior or outer surfaces of a gum base in order to coat the base. The usual gum base can be used, representative materials being jelutong, rubber latex and resins sold under the trade mark VINYLITE, in addition to other usual materials such as plasticizers or softeners, sugar or other suitable carbohydrates such as glucose or sorbitol.

Various adjuvant materials can be incorporated in the dental preparations, provided they do not substantially adversely affect the properties and characteristics thereof. Such materials may be soluble saccharin, flavouring oils (e.g. oils of spearmint, peppermint or wintergreen),

colouring or whitening agents (e.g. titanium dioxide), preservatives (e.g. sodium benzoate), alcohol and menthol. Various other materials can be added such as colouring agents and higher fatty acid amides of amino carboxylic acid compounds, e.g. sodium lauroyl and palmitoyl sarcosides. Other suitable materials are chlorophyllin and various ammoniated ingredients, such as urca, diammonium phosphate and mixtures thereof. Such materials are each usually present in minor amounts of from 0.01% to 3% by weight of the dental preparation.

Example 26:

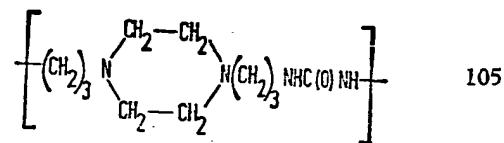
A toothpaste is formed in the normal manner and an aminopolyureylene resin is incorporated therein to provide the following compositions:

	Per cent by weight	
Resin A	0.50, 1.0 and 1.5	
Sodium benzoate	0.15	
Saccharine	0.20	
Sodium N-lauroyl sarcosinate	2.00	85
Insoluble sodium metaphosphate	40.60	
Dicalcium phosphate	4.24	
Titanium dioxide	0.40	90
Na ₂ FPO ₃	0.76	
Gum tragacanth	1.40	
Glycerine (99.3%)	27.10	
Water, colour, flavouring	Balance	
	100.00	95

The foregoing toothpastes are viscous, opaque creams and are effective in improving oral hygiene when used in the usual manner. They are particularly useful in inhibiting calculus formation.

Example 27.

When an aminopolyureylene resin having an average molecular weight of about 5700 and containing the repeating unit



is substituted for Resin A in the composition of Example 26, similar results may be obtained.

Example 28.

A typical chewable dental tablet which is effective against Streptococci A and B and to inhibit calculus formation has the following composition.

Per cent by weight	
Insoluble sodium meta-phosphate	31.69
Talc	0.50
10 Dicalcium phosphate (anhydrous)	4.03
Mannitol	47.30
Starch	3.00
Carboxymethylcellulose (7 m.p.)	1.25
15 Sodium N-lauroyl sarcosinate	2.25
Polyethylene glycol (mol. wt. about 6000)	5.00
20 Saccharine	0.25
Magnesium stearate	1.25
Resin A	1.0
Flavouring, colouring	2.48
	100.00

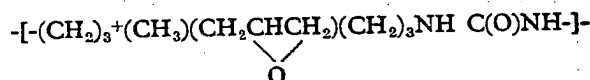
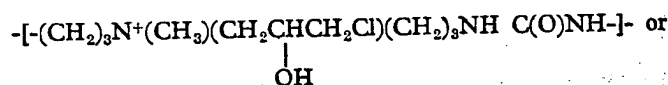
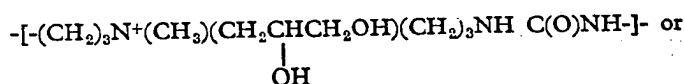
Example 29.

A mouth rinse having the following composition is formed in the usual manner and exhibits the following composition.

Resin A	2.5	
Ethanol	10.0	30
Polyoxyethylene (20) sorbitan monolaurate (Tween 20)	0.4	
Sodium benzoate	0.5	
Sodium saccharinate	0.0065	
Colour	0.32	35
Flavour	0.20	
Water	Balance	
	100.00	

This mouth rinse is effective in inhibiting calculus formation.

When resins having an average molecular weight in the range of 1,000 to 20,000 and a repeating unit of



are substituted for the Resin A in the compositions of Examples 26, 28 and 29 substantially similar results are obtained.

Example 30.

The caries inhibiting properties of the aminopolyureylene resin-containing compositions are shown in the following *in vivo* test. Caries-susceptible, litter-mated hamsters bred either from the Keyes strain or the NIDR (National Institute for Dental Research, U.S.A.) strain in groups of 15 males and 15 females per control group and per each test group were fed a Mitchell cariogenic diet and received constant deionized water. Each day each hamster's teeth were swabbed for 30 seconds by cotton tipped swabs, the control group with water and each test group with a test solution comprising 0.1% by weight of Resin A in deionized water. After six weeks of swabbing the animals were sacrificed, and the defleshed heads were scored by a modi-

fied version of the Keyes scoring method. Mean averages and percentage changes from the control were determined and tested statistically to determine the significance.

Males	36.46	70
Females	14.31	
Mean average	29.17	

The results set forth above indicate the significant effectiveness of the aminopolyureylene resins in reducing caries formation. Thus, these resins are effective to improve oral hygiene by inhibiting calculus and caries formation in the oral cavity as well as inhibiting growth of streptococci therein.

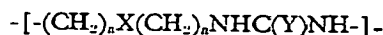
The APU resins are also effective in combination with other caries-inhibiting agents of the thiocarbamate type having the formula $RN^+(CH_3)_2(CH_2)_nOCSN(R_1)_2$ wherein R is an alkyl group of 10 to 18 carbon atoms, n is an integer from 1-4 and R₁ is H or C₁-C₃

alkyl. The proportion of the thiocarbamate in the dental preparation is generally from 0.05% to 5%, preferably 0.1% to 1.0%, by weight.

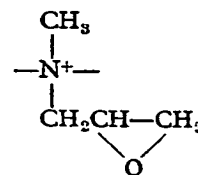
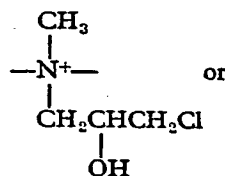
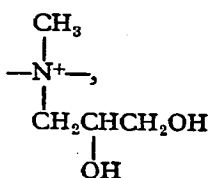
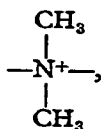
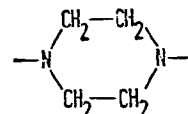
- 5 Generally, the compositions comprising an effective amount of aminopolyureylene resin are intermittently contacted with the oral cavity, e.g. by brushing or swabbing the teeth or rinsing the cavity daily to promote oral hygiene.

WHAT WE CLAIM IS:—

- 10 1. A method of improving the condition of the hair, skin, or oral cavity which comprises applying thereto a composition comprising (I) 0.05 to 10% by weight of a water-soluble aminopolyureylene resin having a molecular weight in the range 300 to 100,000 and having the following repeating unit:—



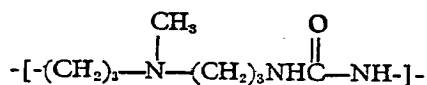
wherein X is $-NH-$, C_{1-22} alkyl
 $-N-$



Y is O or S, and n is 2 or 3;

and (II) a compatible, nontoxic vehicle.

- 20 2. A method in accordance with Claim 1 wherein the repeating unit is



- 25 and the resin is present in the composition in an amount effective to inhibit the growth of *Staphylococcus aureus*, *Pityrosporum ovale*, and/or oral streptococci.

3. A method in accordance with Claim 1 or Claim 2 wherein the resin has an average molecular weight in the range 1,000 to 20,000.

- 30 4. A method in accordance with any of the preceding claims wherein the vehicle comprises an aqueous monohydric or polyhydric alkanol containing 2 or 3 carbon atoms.

5. A method in accordance with any of the preceding claims wherein the vehicle is a cleansing composition comprising from 5% to 99% by weight of water-soluble synthetic organic detergent.

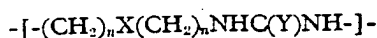
6. A method in accordance with Claim 5 wherein the vehicle is an aqueous cleansing composition containing 5% to 40% by weight of detergent.

7. A method in accordance with any of Claims 1 to 4 wherein the vehicle is an aqueous hair-grooming composition comprising from 0.5% to 65% by weight of a substantially non-volatile organic hair-grooming agent containing a hydroxyl group and having a molecular weight over 75.

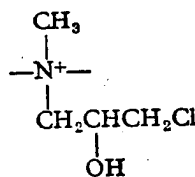
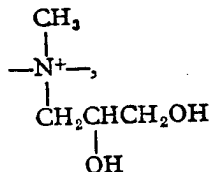
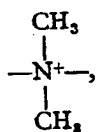
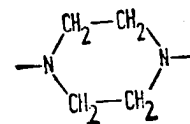
8. A cosmetic composition (as hereinbefore defined) which comprises (I) 0.05% to 10%

by weight of a water-soluble aminopolyureylene resin having a molecular weight in the range 300 to 100,000 and having the following repeating unit:

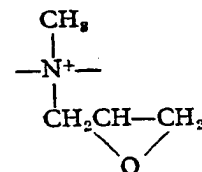
5



wherein X is $-NH-$, C_{1-22} alkyl



or



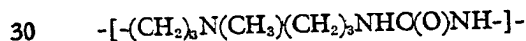
Y is O or S, and n is 2 or 3;

- 10 and (II) 90% to 99.5% by weight of a compatible, nontoxic vehicle which includes at least one member selected from aqueous C_2-C_3 alcohols, water-soluble synthetic organic detergents and water-insoluble polishing agents.

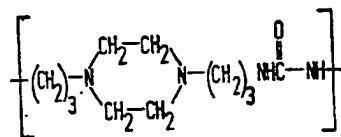
- 15 9. A composition in accordance with Claim 8, for cleaning the hair and skin, wherein the resin is present in an amount of 1% to 10% by weight, and the vehicle comprises 5% to 99% by weight of the composition of compatible, water-soluble synthetic organic detergent.

- 20 10. A composition in accordance with Claim 9 wherein the vehicle is an aqueous vehicle containing 5% to 40% by weight of detergent.

- 25 11. A composition in accordance with Claim 8 or Claim 9 wherein the resin has an average molecular weight in the range 1,000 to 20,000 and the repeating unit is

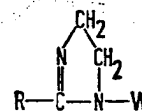


or

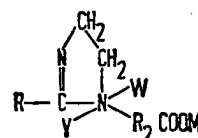


- 35 12. A composition in accordance with any of Claims 9 to 11 wherein the detergent is selected from sodium, potassium, ammonium

and alkylolammonium salts of N-alkyl dimethyl betaines, N-alkyl dimethyl sulphobetaines, N-alkyl amino-carboxylates, C-alkyl imidazole derivatives having the following formulae:



and



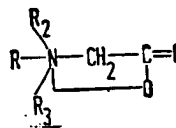
40

wherein W is selected from R_2OH , R_2COOM , and R_2OR_2COOM where R_2 is methylene or ethylene, N-alkyl dimethyl amine oxides, and mixtures thereof, the alkyl group containing from 8 to 18 carbon atoms.

45

13. A composition in accordance with any of Claims 9 to 11 wherein the resin is present in an amount of 0.5% to 5% by weight and the vehicle contains, by weight of the composition, 10% to 30% of water-soluble betaine detergent having the formula

50



wherein R is C₁₀—C₁₆ alkyl, C₁₀—C₁₆ alkyl amidoethyl or C₁₀—C₁₆ alkyl amidopropyl, and R₂ and R₃ are C₁—C₃ alkyl or C₁—C₃ hydroxyalkyl; 1% to 10% of a water-soluble supplementary detergent selected from C₁₀—C₁₈ alkyl sulphates, C₁₀—C₁₈ alkyl amine oxides, C₁₀—C₁₈ acyl sarcosinates, C₁₀—C₁₈ alkyl aminopropionates, C₁₀—C₁₈ alkyl iminodipropionates, C₁₀—C₁₈ alkyl imidazolines and N-(2-hydroxy-C₁₀—C₁₈ alkyl) derivatives of N-methyl taurinate, N-methyl taurinate N-oxide, sarcosinates, sarcosinate-N-oxide and diethanolamine, the salt-forming cation being selected from sodium, potassium, ammonium, and mono-di- and triethanolammonium; and 1% to 10% of a water-soluble nonionic detergent comprising a block copolymer of ethylene oxide and propylene oxide wherein ethylene oxide is 10% to 80% by weight and the molecular weight of this detergent is in the range 1300 to 15,000.

14. A composition in accordance with Claim 13 which contains in addition from 0.2% to 2% by weight of a resinous condensation product of a polyalkylene polyamine with a halohydrin.

15. A composition in accordance with Claim 13 or Claim 14 wherein the nonionic detergent is a mixture of the block copolymer and a condensate of a heteric mixture of oxypropylene and oxyethylene in a ratio of 3:1 to 1:3 on a C₁—C₈ alkanol, the condensate having a molecular weight in the range 600 to 4,000.

16. A composition in accordance with any of Claims 13 to 15 which contains in addition from 1% to 15% of a C₂—C₃ monohydric alcohol.

17. A composition in accordance with any of Claims 13 to 16 which contains 14% to 25% by weight of the betaine detergent, 2% to 6% by weight of the supplementary detergent, 2% to 8% by weight of the nonionic detergent and 1% to 3% of the resin.

18. A composition in accordance with Claim 8, for grooming of the hair, comprising from 0.25% to 10% by weight of the resin and 90% to 99.75% by weight of an aqueous vehicle containing 0.5 to 65% by weight of the composition of a nontoxic, substantially non-volatile hair-grooming agent containing a hydroxyl group and having a molecular weight over 75.

19. A composition in accordance with Claim 18 wherein the vehicle is an aqueous monohydric or polyhydric alkanol containing 2 to 3 carbon atoms.

20. A composition in accordance with Claim 18 or Claim 19 wherein the hair-grooming agent is selected from mineral oil, castor oil, polyhydric alcohols containing 2 or 3 carbon atoms, C₁—C₃ alkyl and hydroxyalkyl esters of C₆—C₁₈ fatty acids, mixed polyethylene glycol polypropylene glycols having a molecular weight in the range 400 to 4,000 and lower

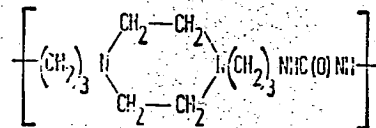
alkoxy polypropylene glycols having a molecular weight greater than 1,000.

21. A composition in accordance with Claim 20 wherein the hair-grooming agent is selected from mixed polyethylene glycol polypropylene glycols having a molecular weight in the range 400 to 4,000 and lower alkoxy-polypropylene glycols having a molecular weight from 1,000 to 2,500 and is present in an amount of 3% to 30% by weight, this agent being solubilized in an aqueous alcoholic medium containing from 30% to 80% by weight of ethanol based upon the total composition.

22. A composition in accordance with any of Claims 18 to 21 wherein the resin has an average molecular weight in the range 1,000 to 20,000 and the repeating unit is



or



23. A composition in accordance with Claim 8, for improving the condition of the oral cavity, comprising an effective amount of the resin in the range 0.05% to 3.0% by weight, and wherein the vehicle is a compatible, nontoxic oral carrier, the composition being effective to improve oral hygiene by inhibiting growth of oral streptococci and inhibiting formation of calculus and caries.

24. An oral composition in accordance with Claim 23 wherein the resin has an average molecular weight in the range of 1,000 to 20,000 and Y is 0.

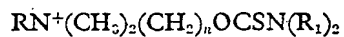
25. An oral composition in accordance with Claim 23 or Claim 24 wherein the carrier comprises from 20% to 95% by weight of the composition of a water-insoluble dental polishing agent.

26. An oral composition in accordance with Claim 25 wherein the carrier comprises, by weight of the composition, 20% to 75% of polishing agent, 15% to 40% of glycerine, propylene glycol or sorbitol humectant, 0.5% to 10% of a gelling agent, and water, the composition being in the form of a dental cream.

27. An oral composition in accordance with Claim 23 or Claim 24 wherein the carrier comprises a flavoured, aqueous alcoholic vehicle containing 4% to 70% of a C₁—C₃ alkanol based on the weight of the composition, the composition being in the form of a mouthwash.

28. An oral composition in accordance with any of Claims 23 to 27 which contains in

addition 0.25% to 5.0% by weight of the composition of a caries-inhibiting thio-carbamate having the formula



- 5 wherein R is an alkyl group of 10 to 18 carbon atoms, n is an integer from 1 to 4 and R_1 is hydrogen or $\text{C}_1\text{—C}_3$ alkyl.

29. An oral composition in accordance with

any of Claims 23 to 28 wherein the repeating unit of the resin is



30. A cosmetic composition (as hereinbefore defined), as claimed in Claim 1 and substantially as described in any of the Examples.

KILBURN & STRODE,
Chartered Patent Agents,
Agents for the Applicants.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1974.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

THIS PAGE BLANK (ICPTO)